

From: Patten, Patricia
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TI Diterpenoids from the roots of *Salvia sclarea*.
AU Ulubelen, Ayhan (1); Sonmez, Ufuk (1); Topcu, Gulacti
CS (1) Fac. Pharm., Univ. Istanbul, 34452 Istanbul Turkey
SO Phytochemistry (Oxford), (1997) Vol. 44, No. 7, pp. 1297-1299.
ISSN: 0031-9422.
DT Article
LA English

TI 2-BETA HYDROXYHAUTRIWAIC-ACID A CLERODANE TYPE DITERPENOID AND OTHER
TERPENOID FROM THREE BACCHARIS SPECIES.
AU ARRIAGA-GINER F J; WOLLENWEBER E; SCHOBBER I; DOSTAL P; BRAUN S
CS DEPARTAMENTO DE QUIMICA ORGANICA, UNIVERSIDAD AUTONOMA DE MADRID,
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BLANCO, E-28034 MADRID, SPAIN.
SO PHYTOCHEMISTRY (OXF), (1986) 25 (3), 719-722.
CODEN: PYTCAS. ISSN: 0031-9422.
FS BA; OLD
LA English

TI Diterpenes from the genus *Amaracus*
AU Passannanti, Salvatore; Paternostro, Mariapia; Piozzi, Franco; Barbagallo,
Claudia
CS Inst. Org. Chem., Univ. Palermo, Palermo, Italy
SO Journal of Natural Products (1984), 47(5), 885-9
CODEN: JNPRDF; ISSN: 0163-3864
DT Journal
LA English

TI A DITERPENE AND FLAVONOID OF BACCHARIS-FLABELLATA.
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SO PHYTOCHEMISTRY (OXF), (1988) 27 (6), 1884-1887.
CODEN: PYTCAS. ISSN: 0031-9422.
FS BA; OLD

(MeOH). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3460, 3490 (OH); 1505, 880 (furan ring); 1743, 1720 (lactone); 1630 (double bond); UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm: 215 (furan ring). ^1H NMR (300 MHz, acetone- d_6 and acetone- d_6 plus D_2O): see Results and Discussion; Overhauser effect, irradiation at C-5 methyl group resulted in 11.1% NOE (C-10 hydroxyl) while irradiation at C-10 hydroxyl resulted in 8.3% NOE of C-5 methyl (see Fig. 1). ^{13}C NMR (75.43 MHz, acetone- d_6): Table 1. High resolution MS: 374.133 $[\text{M}]^+$, (20%, calc. for $\text{C}_{20}\text{H}_{22}\text{O}_7$: 374.1326), 124.0875 (100%, calc. for $\text{C}_8\text{H}_{12}\text{O}$: 124.0888), 95.0492 (22%, calc. for $\text{C}_6\text{H}_8\text{O}$: 95.0496), 94.0417 (41%, calc. for $\text{C}_6\text{H}_8\text{O}$: 94.0418), 81.0345 (45%, calc. for $\text{C}_6\text{H}_8\text{O}$: 81.0340).

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A DITERPENE AND FLAVONOIDS OF *BACCHARIS FLABELLATA*

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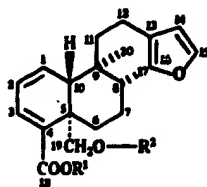
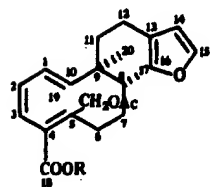
Key Word Index—*Baccharis flabellata*; Compositae; seco-clerodane diterpenoid; nep-clerodane diterpenoid; oleanolic acid; flavonoids.

Abstract—From the aerial parts of *Baccharis flabellata*, two new clerodane type diterpenes were isolated together with oleanolic acid and four known flavonoids. The structures of the new compounds were elucidated by spectroscopic methods.

INTRODUCTION

Following our chemical study of the genus *Baccharis* (Compositae) [1-7], we have now investigated the constituents of *B. flabellata*. From the aerial parts of this plant we have isolated a new 5,10-seco-clerodane diterpenoid

derivative, together with oleanolic acid and the four flavonoids: 5,7,4'-trihydroxy-6,3'-dimethoxyflavone (jaceosidin); 5,3',4'-trihydroxy-6,7-dimethoxyflavone (cirsiliol); 5,7,3',4'-tetrahydroxy-6-methoxyflavone (nepetin); 5,7,4'-trihydroxy-6-methoxyflavone (hispidulin). This paper describes the structural elucidation of the new compounds.



	R
1a	H
1b	Me

	R ¹	R ²
2a	H	Ac
2b	Me	Ac
2c	H	H

DISCUSSION

The HRMS of compound 1a provided the molecular formula $C_{22}H_{28}O_5$. Its IR spectrum showed the presence of a carboxyl group ($3400\text{--}2500\text{ cm}^{-1}$), an ester group ($1740, 1260\text{ cm}^{-1}$), olefinic bonds and a furan ring ($3100, 1630, 1500, 875, 780\text{ cm}^{-1}$). On treatment with diazomethane compound 1a afforded 1b. The ^1H NMR of 1b revealed the existence of a β -substituted furan ring due to the typical resonance pattern arising from three aromatic protons at $\delta 6.36, 7.46$ and 7.36 (Table 1). In addition, the mass spectrum exhibited the expected peaks for a β -ethyl furan side chain at m/z 95 and 81 (base peak) and the ^{13}C NMR spectrum showed signals at $\delta 125.2, 110.5, 138.0$ and 142.0 , assigned to C-13, C-14, C-15 and C-16, respectively, of the assumed β -ethyl furan side chain [8]. The ^1H NMR spectrum also showed signals for a carboxymethyl group as a singlet at $\delta 3.71$, an acetoxymethylene group which appeared as a narrowly doublet at $\delta 3.78$, and a methyl signal at $\delta 2.09$. It also showed two methyl groups, a secondary one at $\delta 0.83$ and a tertiary at $\delta 0.73$. The presence of a methine attached methyl group, which is a frequent feature at C-8 among clerodane-like diterpenes, suggested that 1a might belong to this class of natural products.

The olefinic proton signal pattern showed a narrow *dd* at $\delta 7.13$, a *ddd* at $\delta 5.90$, a *ddd* at $\delta 5.55$ and a *dd* at $\delta 5.26$. These four signals must be attributed to the existence of a triene olefinic system, which can only be accommodated in a 5,10-*seco*-clerodane skeleton as described in 1a. The MS (M^+ at m/z 386) and the ^{13}C NMR spectrum agreed with the proposed structure 1a.

A diagram of the olefinic part of the ^1H NMR spectrum of 1b was reproduced through a program by the spectrum simulator of the Lawrence University (Program NMRSIM, version 1c, 13 December 1974 by R. James S. Evans, Department of Chemistry, Lawrence University).

The ^{13}C NMR spectrum also defined the relative stereochemistry at C-8 and C-9 by comparison of the δ values of the C-17 and C-20 methyl groups with those described for related clerodane diterpenes [9-11]. The values are in agreement with an equatorial methyl group at C-8 as described in 1a.

The other furane diterpenoid 2a had a molecular formula $C_{22}H_{28}O_5$. Its IR and mass spectra (See Experimental), ^1H NMR (Table 1) and ^{13}C NMR (Table 2) spectra showed a β -substituted furan ring. Furthermore, the IR spectrum showed the presence of carboxyl ($3300\text{--}3600\text{ cm}^{-1}$) and ester ($1740, 1260\text{ cm}^{-1}$) groups. On treatment with diazomethane, compound 2a afforded 2b, which showed in the ^1H NMR spectrum a carboxymethylene group which was observed as an AB system at $\delta 4.43$ and 4.13 with the characteristic geminal coupling constant between the methylene protons (10 Hz) and the singlet methyl signal at 1.95 . The chemical shift value of the tertiary and secondary methyl groups were near to those of H-17 and H-20 in 1a and suggested that 2a might belong also to the clerodane-like diterpenoid group. A broad triplet at $\delta 6.96$ was assigned to a β -olefinic proton (H-3) conjugated with a carboxyl ester group. Two olefinic protons at $\delta 6.17$ were assigned to H-1 and H-2 that showed magnetic equivalence. A broad singlet at $\delta 2.58$ was ascribed to the H-10 proton. Spin decoupling experiments confirmed coupling between H-10 and H-1. The small value of the constant suggested a dihedral angle near 90° .

Table 1. ^1H NMR spectra of compounds 1b, 2a, 2b and 2c

H	1b	2a	2b	2c
1	5.55 <i>ddd</i>			
2	5.90 <i>ddd</i>	6.20 <i>br s</i>	6.17 <i>br s</i>	6.16 <i>br s</i>
3	7.13 <i>dd</i>	7.16 <i>br t</i>	6.96 <i>br t</i>	6.70 <i>br t</i>
10	5.26 <i>dd</i>	2.60 <i>br s</i>	2.58 <i>br s</i>	2.60 <i>br s</i>
14	6.36 <i>br s</i>	6.25 <i>br s</i>	6.11 <i>m</i>	6.20 <i>br s</i>
15	7.46 <i>m</i>	7.33 <i>m</i>	7.30 <i>m</i>	7.36 <i>m</i>
16	7.36 <i>m</i>	7.25 <i>m</i>	7.15 <i>m</i>	7.26 <i>m</i>
17	0.83 <i>d</i>	0.86 <i>d</i>	0.80 <i>d</i>	0.86 <i>d</i>
19	Ha 3.93 <i>d</i> ; Hb 3.63 <i>d</i>	Ha 4.44 <i>d</i> ; Hb 4.13 <i>d</i>	Ha 4.43 <i>d</i> ; Hb 4.13 <i>d</i>	3.80 <i>s</i>
20	0.73 <i>s</i>	0.85 <i>s</i>	0.85 <i>s</i>	0.85 <i>s</i>
COOMe	3.71 <i>s</i>	—	3.71 <i>s</i>	—
Me-CO.O	2.09 <i>s</i>	1.93 <i>s</i>	1.95 <i>s</i>	—

J (Hz) 1b: 1,2 = 12; 1,10 = 5; 1,3 = 1; 2,3 = 1.7; 2,10 = 1.30; 19a, 19b = 9 Hz; 17,8 = 6. 2a: 19a, 19b = 10 Hz; 17,8 = 5.5. 2b: 19a, 19b = 10 Hz; 17,8 = 5.5. 2c: 17,8 = 5.5.

Table 2. ^{13}C NMR spectra of compounds 1b, 2a and 2b

C	1b	2a	2b
1			
2	142.5	136.3	134.2
3	127.9	124.7	124.7
4	126.3		
5	131.8	135.6	133.7
10		47.9	47.8
4	119.5	134.5	135.6
5	129.8	38.2	38.1
6	35.6	30.9	30.9
7	28.3	26.8	26.8
8	35.1	35.3	35.3
9	37.9	41.0	41.0
11	37.3	37.7	37.6
12	19.2	18.7	19.6
13	125.2	124.8	124.9
14	110.5	110.6	110.7
15	138.0	138.2	138.6
16	142.0	142.5	142.5
17	13.5	15.4	15.3
18	167.1	172.4	170.8
19	62.0	62.1	62.2
20	18.1	19.7	18.0
COOMe	51.6		51.1
Me-COO	20.3	20.6	20.6
Me-C=O	170.7	170.9	167.0

The UV absorption exhibited the expected value for such a diene system ($\lambda_{\text{max}}^{\text{MeOH}}$ nm 298, $\lambda_{\text{max}}^{\text{n-hexane}}$ nm 292). The ^{13}C NMR spectrum of this compound was in agreement with these assignments and was made on the basis of the observed multiplicities (APT) and of the comparison with reported ^{13}C NMR spectral data of similar derivatives [12]. The chemical shifts of C-17 and C-20, as well as those of 1a, also defined the relative configuration of C-8 and C-9 [9-11]. The large negative optical rotation (See Experimental) suggests that the absolute configuration of 2a was that of hautriwaic acid [12].

Finally the treatment of 2a with methanolic KOH yielded 2c. The spectroscopic data of the latter (^1H NMR, IR and UV) led us to identify it as a clerodane, already found in *Dodonaea attenuata* [13].

EXPERIMENTAL

^{13}C and ^1H NMR spectra were recorded in CDCl_3 ; M spectra were determined utilizing a Varian Mat 112 S spectrometer at 70 eV and 0.7 mA.

Plant material. *Baccharis flabellata* was collected in March and September 1985 in Tucuman and San Luis respectively. Voucher specimens are kept at the Herbaria (VMSL 2862; UNSL 34).

Extraction and isolation. The air-dried plant material (1.2 kg) was extracted with hot MeOH (3 x 3). The extract was concentrated, then, H_2O was added (10:20 and 30%) and partitioned between n-hexane, CCl_4 , CHCl_3 and EtOAc, respectively. The CHCl_3 was evaporated and the residue (45 gr) was subjected to CC on silica gel 60 G and developed successively with C_6H_6 and

C_6H_6 containing increasing proportions of EtOAc. Fractions of 100 ml were taken and combined upon TLC monitoring, yielding the following compounds in order of elution: 1a (80 mg); 2a (500 mg); oleanolic acid (4 g) and a mixture of flavonoids. The mixture of flavonoids was rechromatographed first on a silica gel column (120 g) where it was eluted with C_6H_6 -EtOAc (5:5) and then on a Sephadex LH-20, where it was eluted with MeOH, yielding: 5,7,4'-trihydroxy-6,3'-dimethoxy flavone; 5,3,4'-trihydroxy-6,7-dimethoxy flavone; 5,7,3,4'-tetrahydroxy-6-methoxy flavone; 5,7,4'-trihydroxy-6-methoxy flavone. The previously known flavonoids were identified by comparison of their spectroscopic (^1H NMR, UV and MS) properties with those reported in the literature [14, 15].

Compound 1a. Colourless oil, IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3400, 3100, 2500, 1740, 1630, 1500, 1260, 875, 780. HRMS calc. for $\text{C}_{22}\text{H}_{28}\text{O}_3$, MW: 372.1937, found M, (MS) 372.1929. 80 mg 1a were dissolved in dry Et_2O , and CH_2N_2 was added slowly, following the usual work-up to give 75 mg of 1b, colourless oil. MS m/z (rel. int.): 386 [M] $^+$ (2); 343 (4); 326 (5); 313 (10); 295 (8); 283 (14); 231 (10); 149 (35); 95 (37); 91 (27); 81 (100). For ^1H NMR data, see Table 1. ^{13}C NMR data are compiled in Table 2. $\lambda_{\text{max}}^{\text{MeOH}}$ nm 225;

$[\alpha]_D^{25}$	589	578	546	436
	-33.84	-35.2	-40.57	-88.82

(CHCl_3 ; c 4.5)

Compound 2a. Colourless oil. HRMS calc. for $\text{C}_{22}\text{H}_{28}\text{O}_3$, MW: 372.1937, found M, (MS) 372.1933. IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3600-3300, 1740, 1680, 875, 780. The ^1H and ^{13}C NMR data of 2a are shown in Tables 1 and 2, respectively. Compound 2a was esterified with CH_2N_2 in Et_2O to give 2b as a colourless oil. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm 298, $\lambda_{\text{max}}^{\text{n-hexane}}$ nm 292.

$[\alpha]_D^{25}$	589	578	546	436
	-122.31	-128.71	-152.33	-333.54

(CHCl_3 ; c 0.619)

MS m/z (rel. int.): 386 [M] $^+$ (14), 354 [M - MeOH] $^+$ (28), 313 [M - 73] $^+$ (75), 281 [354 - 73] $^+$ (44.2), 95 [$\text{C}_6\text{H}_5\text{O}$] $^+$ (27.1), 81 [$\text{C}_6\text{H}_5\text{O}$] $^+$ (100).

See Tables 1 and 2 for ^1H and ^{13}C NMR data respectively. The treatment of 2a with methanolic KOH gave 2c. See ^1H NMR in Table 1.

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TRITERPENES FROM *CIGARRILLA MEXICANA**

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Key Word Index—*Cigarrilla mexicana*; Rubiaceae; cucurbitacin E; isocucurbitacin B; epi-isocucurbitacin B; 3 β -23-dihydroxy-urs-12-en-28-oic acid; cucurbitacins.

Abstract—From the aerial parts of *Cigarrilla mexicana* 3 β , 23-dihydroxy-urs-12-en-28-oic acid, a new natural product, has been isolated together with the already known cucurbitacin E, isocucurbitacin B, epi-isocucurbitacin B, ursolic and oleanoic acids. The structure of the new substance was established by chemical and spectroscopic means.

INTRODUCTION

In continuation of our work on Mexican plants used in Traditional Medicine, we have now investigated aerial parts of *Cigarrilla mexicana* (Zucc. et Martius ex DC) Aiello (Rubiaceae), known in Mexico as cigarro, cigarrilla or cacaloxochilt. *Cigarrilla* is a monotypic species endemic to Hidalgo, Querétaro and San Luis Potosí, Mexico. The aerial parts, intensely bitter, are used locally for the treatment of amebiasis and as an emetic [1; Lorence, D., unpublished results]. No previous chemical work on the plant has been described.

RESULTS AND DISCUSSION

After repeated column chromatography on silica gel the concentrated methanolic extract of the defatted aerial parts of *C. mexicana* afforded the known compounds

cucurbitacin E, isocucurbitacin B, epi-isocucurbitacin B as well as oleanoic and ursolic acids. In addition, a new natural ursene 1, was isolated in 0.006% yield.

Compound 1, C₃₀H₄₈O₄, mp 266–268°, was obtained as colourless needles. Treatment of 1 with pyridine-acetic anhydride afforded diacetate 1b and methylation with diazomethane yielded methyl ester 1a. Finally, treatment with acetone-H₂SO₄ gave the stable acetone 1c, thus indicating the presence of a 1–3 or 1–2 glycol moiety in the molecule.

The electron impact mass spectrum showed ions at *m/z* 248, (base), 223, 205 [223–H₂O] and 203 [248–COOH], the typical retro-Diels–Alder fragments of a triterpene acid of the Δ^{12} oleanene or ursene type [2, 3]. Furthermore the peaks at *m/z* 223 and 205 indicated that 1 had two hydroxyl groups on the ring A and/or ring B [4].

The ¹H NMR spectrum of 1 (Table 1) exhibited signals for two secondary methyl groups, four methyl singlets, one proton doublet (*J* = 11 Hz) at δ 2.17 (H-18) and one proton multiplet at δ 5.20 (H-12), as expected for an urs-12-ene skeleton [5–7]. Also, it showed an AB system (δ 3.29, 3.65, *J* = 11 Hz), which shifted downfield on acylation in 1b, indicative of the presence of an equatorial hydroxy methylene group attached to an asymmetric

*Part 4 in the series 'Chemical Studies on Mexican Plants used in Traditional Medicine'. For Part 3 see R. Mata et al. (1987) *J. Nat. Prod.* **50**, 866.

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